Fabrication and Characterization of LiFePO$_4$ Nanotubes by a Sol-gel-AAO Template Process

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The LiFePO$_4$ nanotubes were successfully fabricated by a sol-gel method with porous anodic aluminum oxide as the template. Transmission electron microscopy and scanning electron microscopy showed that the synthesized LiFePO$_4$ nanotubes were monodispersed and parallel to one another. Selected area electron diffraction pattern, X-ray diffraction and X-ray photoelectron spectroscopy investigations jointly demonstrated that the synthesized LiFePO$_4$ nanotubes were pure olivine structure. This approach offered a potentially way for fabricating ordered LiFePO$_4$ nanotubes at room temperature and ambient conditions, which might be expected to find promising application as a new cathode material in lithium ion battery.

Key words: LiFePO$_4$, AAO template, Sol-gel, Lithium ion battery

I. INTRODUCTION

There has been rapid progress in the development of one-dimension nanostructure materials, due to their special electronic, magnetic, optical and mechanical properties in comparison with their bulk counterparts [1-4]. Nanowires, nanorods and nanobelts constitute an important class of one-dimension nanostructures, which provide models to study the relationship among electronic transport, optical, and other properties such as dimensionality and size confinement [5]. Many strategies for the fabrication of one-dimension nanostructure materials have been developed, such as vapor-liquid-solid (VLS) growth [6], oxide-assisted growth [7], catalytic CVD growth [8], template synthesis [9], etc. Among these techniques, template method is a convenient and inexpensive technique [10-15]. It has been demonstrated that the physical and chemical properties of the prepared materials are tunable via controlling their size and shape that are dominated by the template and experiment parameters [16]. Various templates including anodic porous alumina, polymer and nanochannel glass templates are available [17]. Specifically, anodic aluminum oxide (AAO) templates are often used for synthesizing high surface area and ordered one-dimension nanostructure materials because AAO templates possess very regular and highly anisotropic porous structures and the pores in these membranes have little or no tilt with respect to the surface normal resulting in an isolating, non-connecting pore structures [14].

Nowadays, one-dimension nanostructure materials used in the lithium ion battery have been extensively studied, in which cathode materials have been shed much light on [17-19]. As a candidate of cathode materials, olivine structure LiFePO$_4$ has extraordinary advantages such as low-cost, environmental benefits and exhibits good thermal stability in the highly charged state as well as a relatively large theoretical specific capacity. But LiFePO$_4$ has a vital drawback, its inherently low electronic conductivity, which results in poor rate capacity. As we all know, the cathode electrical conductivity and lithium ion diffusion coefficient are two of the most important issues responsible for the rate capability of batteries [20]. Many approaches have been considered to overcome LiFePO$_4$ poor conductivity, such as doping transition metal ions [20], adding a conductive material [21, 22], carbon coating and cosynthesizing with carbon by solid-state method [21, 23-25]. Yamada et al. reported that the increase in the specific surface area resulted from very fine and uniform particles might be a good solution to obtain excellent electrochemical cycle performance [26]. However, large particle size and poor particle size distribution (PSD) of LiFePO$_4$ powder is usually obtained in a solid-state method. Therefore, it is critical to find a method by which LiFePO$_4$ can be synthesized with small grain size and high electronic conductivity for the improvement of its rate capability. In this work, LiFePO$_4$ nanotubes are synthesized using a sol-gel method within AAO template pores. The structure and composition of the synthesized LiFePO$_4$ nanotube materials are characterized as well, which are expected to be used potentially as a new cathode material in lithium ion battery.

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II. EXPERIMENTS

A sol-gel method was developed to synthesize LiFePO$_4$ nanotubes precursor sol, and citric acid was employed as a chelating agent and a carbon source in the developed process [20]. Stoichiometric amounts of ferrous sulfate and lithium nitrate were dissolved in 20 mL deionized water, then an appropriate amount of citric acid solution (66wt%) was added dropwise with continuous stirring. After that, a saturated solution of ammonium dihydrogen phosphate (53wt%) was added to this solution. Under continuous stirring, the mixtures were heated at 60°C for 4 h until a transparent sol was obtained. The sol was very stable at room temperature and no precipitate was observed even for a long time. In this experiment, the molar ratio of chelating agent to the total metal ion was 1:1, and the molar ratio of Fe:Li:P=1:1:1. The cleaned alumina membrane (Whatman anodisc, diameter of 47 mm) with pore diameter of approximate 200 nm, porosity of about 43%, was dipped into the prepared sol. Then the AAO template and sol system were transferred to a vacuum drier. After a certain time, the membrane was removed, and the excess sol on the membrane surface was wiped off with a laboratory tissue. Finally, the membrane was placed in oven to dry at 60°C in air for 10 h followed by a calcination at 550°C for 2 h in argon atmosphere in a tube-stove, which resulted in the formation of LiFePO$_4$ nanotubes inside the pores of the AAO template.

The morphology, composition and crystallography of the LiFePO$_4$ nanotubes were characterized. TEM images were obtained on a HITACHI-600 microscope to observe the morphology and agglomeration degree of the synthesized nanotubes. The alumina template membrane was removed by dissolving with 3 mol/L NaOH, and then diluted with deionized water. Droplets of solution containing LiFePO$_4$ nanotubes were dropped onto the copper grids for TEM observation. SEM images were recorded with JSM-5600LV microscope. For SEM sample, the alumina template membrane was attached on a Cu cylinder. Then, a few droplets of 3 mol/L NaOH were dropped onto the sample to dissolve membrane partially, then the samples were sputter-coated with gold prior to observation. The phase structure of the synthesized LiFePO$_4$ nanotubes with template membrane was determined on a D/Max-RB X-ray diffractometer (Rigaku Corp., Tokyo, Japan) with Cu-Kα radiation at a scanning step size of 2θ=0.017°. The data were acquired in the 2θ range of 10° to 80°. The chemical states of typical elements of the nanotubes with template membrane were analyzed on a PHI-5702 multi-functional X-ray photoelectron spectroscopy (Physical Electronics, USA) operating with Al-Kα irradiation (hv=1486.6 eV) at a pass energy of 29.35 eV. The binding energy of contaminated carbon (Cls: 284.8 eV) was used as the reference and the resolution is about ±0.3 eV.

III. RESULTS AND DISCUSSION

The TEM image of LiFePO$_4$ nanotubes formed within the AAO template is shown in Fig.1.

Figure 1(a) displays a large number of LiFePO$_4$ nanotubes, from which we can see that these nanotubes contact, across and overlap each other and the wall thickness of the nanotubes is about 25 nm. Li et al. have reported that the growth mechanism of nanowires inside AAO template via a sol-gel process is the nanoparticles deposition process in the pores of the AAO template, so do the LiFePO$_4$ nanotubes grown within AAO template [27]. It can also be found to some extent from Fig.1(a) that there are some nanoparticles inside some nanotubes, which is perhaps attributed to the fact that ultrasonic treatment of TEM samples that probably destroy the nanotubes structure partially. The corresponding selected area electron diffraction (SAED) pattern taken from one of the above mentioned LiFePO$_4$ nanotubes is shown in Fig.1(b). The diffraction rings, from inner to outer, correspond to the (011), (121), (200), (131), (140) and (511) diffraction planes of orthorhombic LiFePO$_4$. So, it can be concluded that the synthesized LiFePO$_4$ nanotubes have well-defined olivine structure and are polycrystalline. This is identical with the results reported by Lin et al. [28,29]. They have demonstrated that the nanotubes or nanowires
fabricated by the sol-gel method with AAO templates are polycrystalline.

The typical SEM images of synthesized LiFePO$_4$ nanotube arrays grown within AAO template are given in Fig.2. These images reveal that the nanotubes are parallel to one another, uniformly distributed and highly-ordered. Figure 2(a) shows a part of panorama of LiFePO$_4$ nanotubes which shows that the alumina matrix is almost dissolved completely, and the synthesized nanotubes adhere together only at bottom due to the residual alumina membrane. A cross-sectional segment of LiFePO$_4$ nanotube arrays is shown in Fig.2(b), in which the alumina matrix of the AAO template has been dissolved away partially. It can be obviously seen that the orientation of the nanotubes is consistent with that of AAO template pores. Figure 2(c) presents a cluster of LiFePO$_4$ nanotubes with fiber-brush aspect and compact alignment, the length of the nanotubes is about 60 μm. From the cross section of the nanotube arrays (Fig.2(d)), it can be observed that the synthesized nanotubes have tubular structure with uniform outer diameter and wall thickness of about 25 nm, which is greatly consistent with the result of TEM analysis.

The XRD pattern of the synthesized LiFePO$_4$ nanotube arrays within the AAO template was also characterized by XPS measurements. The XPS survey scan spectrum of the prepared sample is shown in Fig.4. It is clear that the signals of Li, Fe, P, Al and O are present in the spectrum, and C1s is also detected at 284.8 eV, which is assigned to the ubiquitous adventitious carbon. Figure 5 shows the high resolution XPS spectra of Li1s, Fe2p, P2p, O1s and Al2p in the LiFePO$_4$/AAO composite. The peak of Li1s at 55.4 eV (Fig.5(a)) indicates that Li exists in the state of Li$^+$. In the case of Fe, the intensity of Fe2p$_1/2$ signal is usually lower if the oxidation state of Fe is +2, and the ratio of high binding energy intensity (Fe2p$_1/2$) to low binding energy intensity (Fe2p$_3/2$) is less than 0.55. Furthermore, Huang et al. have reported that a shake-up peak usually exists beside the main peak of Fe2p, and the distance of the two peaks is smaller than 4 eV in terms of Fe(II) [30]. In our measurement, the Fe2p characteristic signals in the prepared sample are located at 711.8 eV (Fe2p$_3/2$) and 724.3 eV (Fe2p$_1/2$), respectively (Fig.5(b)), in agreement with Teja et al.’s report that the Fe2p$_3/2$ located at 711.85 eV [31]. The ratio of high binding energy intensity (Fe2p$_1/2$) to low binding energy intensity (Fe2p$_3/2$) is 0.36. Beside the
FIG. 3 XRD pattern of LiFePO$_4$ nanotube arrays with AAO template.

FIG. 4 XPS survey spectrum of the LiFePO$_4$/alumina template composite membrane.

FIG. 5 High resolution XPS spectra of Li1s(a), Fe2p (b), P2p (c), O1s (d) and Al2p (e) in the LiFePO$_4$/AAO composite.

Fe2p$_{3/2}$ peak, there is a shake-up peak at 714.7 eV, and the space of two peaks is 2.9 eV. Therefore, it can be confirmed that the average oxidation state of Fe is +2. The P2p signal appeared at 133.9 eV corresponding to P$^{5+}$ (Fig.5(c)). The line shape of the core levels O1s and Al2p are Gaussian-like with a binding energy of 531.2 eV (Fig.5(d)) and 74.5 eV (Fig.5(e)), corresponding to O$^{2-}$ and Al$^{3+}$, respectively. It is well known that XPS measurement can be used to quantify the proportion of the elements existed in the analyzed sam-
ple. For the quantitative analysis of O in the synthesized LiFePO$_4$, the part corresponding to Al$_2$O$_3$ should be deducted. We used the relative sensitivity factors method (RSFM) to calculate the number of every atom and the calculation result confirms that the synthesized product is in the form of LiFePO$_4$ and more likely to stoichiometric olivine material.

IV. CONCLUSION

In summary, LiFePO$_4$ nanotubes with porous anodic aluminum oxide (AAO) as the template were prepared via a sol-gel method. The precursor sol contains lithium nitrate, ferrous sulfate and ammonium dihydrogen phosphate. Citric acid is employed not only as a chelating agent but also a carbon source in the sintering process. TEM and SEM characterization show that the synthesized LiFePO$_4$ nanotubes are monodispersed and high-ordered arrays, while XRD along with XPS investigations demonstrate that the synthesized LiFePO$_4$ nanotubes are pure olivine structure. This approach offers a potentially way for fabricating ordered LiFePO$_4$ nanotubes at room temperature and ambient conditions, which may be expected to be used as a potential technology for fabricating new cathode materials in lithium ion battery.

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